Chem 338

Homework Set #11 solutions December 5, 2001

From Atkins: 11.7, 11.9, 11.12 and 11.24 (extra)

11.7) Two radioactive nuclides decay by successive 1st-order processes:

$$X \xrightarrow{22.5\ d} Y \xrightarrow{33.0\ d} Z$$

At what stage after X is first formed will Y be most abundant?

Working with Eq.(11.4b) and Fig. 11.3, one obtains Eq.(11.5) by taking the 1st derivative of Eq.(11.4b) with respect to the concentration of the intermediate and setting this result equal to zero. This then locates the maximum in the [I] vs. time function in Fig. 11.3.

$$t = \frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2} \qquad (11.5)$$

From the half-lives of each step and knowing that they are both 1st-order reactions,

$$t_{1/2} = \frac{\ln 2}{k}, \quad \text{and} \quad k_1 = \frac{\ln 2}{22.5\text{d}} = 0.030807\ \text{d}^{-1}, \quad k_2 = \frac{\ln 2}{33.0\text{d}} = 0.021004\ \text{d}^{-1}$$

so, $$t = \frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2} = \frac{1}{0.030807 - 0.021004} \ln \frac{0.03087}{0.021004}$$

$$= 39.1 \text{ days}$$

11.9) The reaction mechanism

$A_2 \rightarrow 2A$ (fast)

$A + B \rightarrow P$ (slow)

involves an intermediate A. Deduce the rate law for the formation of P.

For the 2nd step: $$\frac{d[\text{P}]}{dt} = k_2[\text{A}][\text{B}]$$

The rate law for the 2nd step in terms of the production of P is what we will work with to obtain the overall rate law (since this is also in terms of production of P)

To get rid of the intermediate A in this rate law, we could use the steady state approximation, but you'd find that you'd get a nasty looking quadratic in [A].

Alternatively, since the slow step (2nd) is preceeded by a fast step (1st), we can safely assume that the 1st step will reach equilibrium (a "pre-equilibrium")

From step 1: $K = \frac{[\mathrm{A}]^2}{[\mathrm{A}_2]}$, and thus $[\mathrm{A}] = K^{\frac{1}{2}}[\mathrm{A}_2]^{\frac{1}{2}}$

Substituting into the rate law above, $\frac{d[\mathrm{P}]}{dt} = k_2 K^{\frac{1}{2}}[\mathrm{A}_2]^{\frac{1}{2}}[\mathrm{B}]$

11.12) The condensation reaction of acetone, $(CH_3)_2CO$, in aqueous solution is catalyzed by bases, B, which react reversibly with acetone to form the carbanion $C_3H_5O^-$. The carbanion then reacts with a molecule of acetone to give the product. A simplified version of the mechanism is:

(1) $AH + B \rightarrow BH^+ + A^-$

(2) $A^- + BH^+ \rightarrow AH + B$

(3) $A^- + HA \rightarrow$ product

where AH or HA stands for acetone and A^- is its carbanion. Use the steady state approximation to find the concentration of the carbanion and derive the rate equation for the formation of the product.

Write the rate law for each step : (note: you have a choice, but I'll write them in terms of the carbanion, since we're going to use the ss approximation to get rid of it)

(1) $\frac{d[A^-]}{dt} = k_1[AH][B]$

(2) $-\frac{d[A^-]}{dt} = k_2[A^-][BH^+]$

(3) $-\frac{d[A^-]}{dt} = k_3[A^-][HA] \quad = \frac{d[\text{product}]}{dt}$

Employ the steady state approximation for A^-:

$$\frac{d[A^-]}{dt} \approx 0 = k_1[AH][B] - k_2[A^-][BH^+] - k_3[A^-][HA]$$

Solving for $[A^-]$: $[A^-]_{ss} = \frac{k_1[AH][B]}{k_2[BH^+] + k_3[HA]}$

Substituting into the rate equation for formation of product in step (3):

$$\frac{d[\text{product}]}{dt} = \frac{k_1 k_3 [AH]^2[B]}{k_2[BH^+] + k_3[HA]}$$

11.29) In a photochemical reaction A → 2B + C, the overall quantum yield with 500 nm light is 2.1×10^2 mol einstein^{-1}. After exposure of 300 mmol A to the light, 2.15 mmol B is formed. How many photons were absorbed by A ?

The definition of the overall quantum yield is: $\Phi = \frac{\#\ \text{moles that react}}{\text{einsteins of radiation absorbed}}$

Based on the stoichiometry of the reaction, the formation of 2.15 mmol of B means that $\frac{2.15}{2}$ mmol of A reacted.

Hence, $\Phi = 2.1\times10^2 = \frac{2.15\times10^{-3}/2}{\text{einsteins absorbed}}$

$$\text{einsteins absorbed} = \frac{2.15\times10^{-3}/2}{2.1\times10^2} = 5.119\times10^{-6}\ \text{einsteins}$$

$$\#\ \text{photons absorbed} = 5.119\times10^{-6}\ \text{einsteins} \times \frac{6.02214\times10^{23}\ \text{photons}}{\text{einstein}}$$

$$= 3.1\times10^{18}\ \text{photons absorbed}$$